the thickness and ambient temperature of the thrust sheet in the western part of the Blue Ridge at the time it was emplaced. This factor would affect any rocks beneath the thrust sheet regardless of their age. Assuming present thicknesses and a reasonable interpretation of southern and central Appalachian structure (*17*), temperatures would be too high today beneath most of the sheet for hydrocarbons to survive (Fig. 3), unless there is some process capable of creating and maintaining abnormally low temperature and pressure conditions over hundreds of millions of years. This is unlikely in light of observations in areas where deeply eroded crystalline thrust sheets occur, such as in the Scandinavian Caledonides. One of the best examples is near Åre in Sweden, where granulite facies (Caledonian metamorphism) rocks occur in the highest thrust sheet at the top of the mountain Åreskutan. However, some 1700 m lower, near the base of the mountain, Lower Silurian limestones contain identifiable crinoid fragments (*18*). It is obvious that metamorphism occurred before emplacement of the thrust sheets. However, despite the fact that fossils occur in the limestone near the base of the mountain, this limestone is penetratively deformed and metamorphosed at least to the greenschist facies. Minimal restored burial depth of the fossiliferous rocks to the elevation of the present topography is less than 1 km. The thickness of the thrust pile must have been several times this at the time of emplacement. The important conclusion both there and in the Appalachians is that the higher the metamorphic grade of the highest grade rocks in a pile of thrust sheets, the higher the metamorphic grade of the lowest grade rocks beneath the sheets, provided emplacement of the thrust sheets is related to one or more of the metamorphic and thermal events producing the high grade rocks.

ROBERT D. HATCHER, JR.
Department of Geology, University of South Carolina, Columbia 29208

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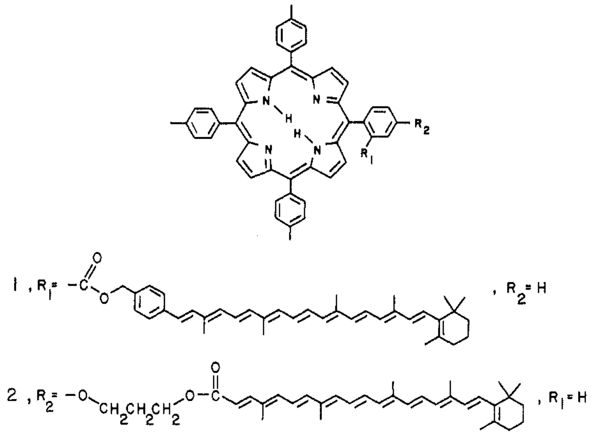
Photoprotection by Carotenoids During Photosynthesis: Motional Dependence of Intramolecular Energy Transfer

Abstract. *A new carotenoporphyrin has been prepared in which a synthetic carotenoid is joined to a tetraarylporphyrin through a flexible trimethylene linkage. This molecule exists primarily in an extended conformation with the carotenoid chromophore far from the porphyrin π-electron system. In benzene solution, where large-amplitude molecular motions are rapid, the molecule can momentarily assume less stable conformations which favor triplet energy transfer, and quenching of the porphyrin triplet by the carotenoid is fast. In a polystyrene matrix or frozen glass such motions are slow, and energy transfer cannot compete with other pathways for depopulating the triplet state. These observations help establish the requirements for biological photoprotection.*

Carotenoid polyenes serve at least two functions in the photosynthetic apparatus of green plants. They are useful as antenna pigments which absorb light in regions of the spectrum where chlorophylls are not efficient and transfer excitation energy to the chlorophyll singlet manifold. They are vital as photoprotective agents which mitigate the harmful effects of singlet oxygen. Synthetic carotenoporphyrins such as **1** can serve as model systems which define the structural requisites for both photoprotection and antenna function (*1*–*3*). We now report studies of a new carotenoporphyrin showing that the dynamics of the molecule, as well as the static structure, play a crucial role in the photophysical events basic to the biological functions of these pigments.



In green plants the major potential source of singlet oxygen is sensitization by chlorophyll triplet states. Thus carotenoid polyenes can provide photoprotection by quenching the chlorophyll triplets before they can react with oxygen. In benzene solution at ambient temperatures, triplet energy transfer from the porphyrin chromophore of **1** to the carotenoid occurs with 100 percent efficiency and the porphyrin triplet state is completely quenched within ~ 25 nsec (*3*). Thus the porphyrin triplet lifetime is too short to allow singlet oxygen production under atmospheric conditions, and photoprotection in **1** is completely effective (*3*). Using similar techniques, we have determined that triplet-triplet energy transfer also occurs on the nanosecond time scale when **1** is irradiated in a deoxygenated polystyrene or cellulose triacetate matrix.

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Using synthetic methods similar to those described earlier (*1*, *2*), we prepared the new carotenoporphyrin, **2**, in which the carotenoid polyene is joined to the porphyrin ring through a flexible methylene chain (*4*). In deoxygenated benzene solution, triplet-triplet energy transfer in **2** is also rapid. Studies of $T_1 \rightarrow T_n$ absorption, where T_1 and T_n are the first and a higher triplet state, respectively, were carried out following excitation by a 353-nm laser flash of 25-nsec duration (*3*). A typical porphyrin $T_1 \rightarrow T_n$ absorption spectrum ($\lambda_{max} \sim 440$ nm), accompanied by ground-state bleaching, was observed immediately after the flash (Fig. 1). This spectrum decayed with a lifetime $\tau = 80$ nsec (Fig. 2). A typical carotenoid $T_1 \rightarrow T_n$ spectrum ($\lambda_{max} \sim 540$ nm) grew in at the same rate (accompanied by ground-state bleaching) and decayed with $\tau = 2.4$ μsec (*5*). This quenching of the porphyrin triplet state must be intramolecular because it occurs much more rapidly than is possible for intermolecular triplet energy transfer at this concentration. The rapid quenching of the porphyrin triplet suggests that the carotenoid moiety of **2** could provide substantial photoprotection in solution. Indeed, singlet oxygen studies with **2** as sensitizer in the system described previously (*3*) show a level of photoprotection approximately 90 percent that of **1**.

The results for **2** dissolved in a deoxygenated polystyrene or cellulose triacetate matrix are strikingly different. Flash experiments similar to those described above again yielded the porphyrin $T_1 \rightarrow T_n$ absorption spectrum immediately after the flash. However, this spectrum persisted, and no carotenoid $T_1 \rightarrow T_n$ absorption spectrum (or concomitant carotenoid ground-state bleaching) was observed. The porphyrin triplet lifetime was measured with a flash apparatus (2 msec) and, in a separate experiment, by measuring the phase shift of the $T_1 \rightarrow T_n$ absorption signal as a function of the modulation frequency of a chopped pump beam from a xenon arc lamp and monochromator (2 msec). Although the measured lifetime was sensitive to traces of oxygen in the plastic, the values obtained are typical for unquenched porphyrin triplets. Thus with **2** triplet-triplet energy transfer in the plastic matrix does not occur. A similar result was obtained with a dilute solution of **2** in EPA glass at 77 K (not deoxygenated), where the porphyrin triplet lifetime was ~ 3 msec.

This dichotomy of behavior for **1** and **2** can be understood as follows. Triplet energy transfer occurs by an electron exchange mechanism. To be effective, such a mechanism requires very close approach of the carotenoid and porphyrin π-electron systems. In solution, **1** was shown by ^{1}H nuclear magnetic resonance (NMR) measurements of porphyrin ring current–induced chemical shift changes (*2*) to assume a folded conformation in which the carotenoid backbone is stacked ~ 4 Å above the porphyrin plane. Thus the two π-electron systems are in intimate contact, and quenching of the porphyrin triplet by the carotenoid is very rapid. The fast triplet transfer observed for **1** in the polystyrene matrix is good evidence that a folded conformation persists under these conditions. Carotenoporphyrin **2**, on the other hand, exists in an extended conformation in benzene solution without close approach of the π-electron systems. This is clear from the ^{1}H NMR spectrum; the carotenoid protons do not experience significant shielding by the porphyrin ring current. However, because **2** is flexible it can undergo large excursions from its most stable conformation during the lifetime of the porphyrin triplet, and the carotenoid chromophore can approach the porphyrin π system so that triplet-triplet transfer is enhanced. It is reasonable to assume that **2** also adopts an extended conformation in plastic or EPA glass. However, in these media the large-amplitude excursions are restricted by solvent viscosity, and the porphyrin triplet decays by nonradiative processes and phosphorescence before triplet energy transfer can occur.

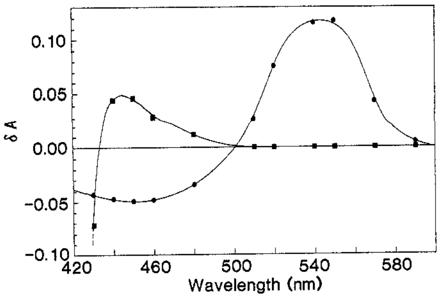

Fig. 1. Transient absorbance changes (δ*A*) immediately (■) and 200 nsec (●) after 353-nm laser flash photolysis of a $4.3 \times 10^{-6}M$ solution of **2** in deoxygenated benzene.

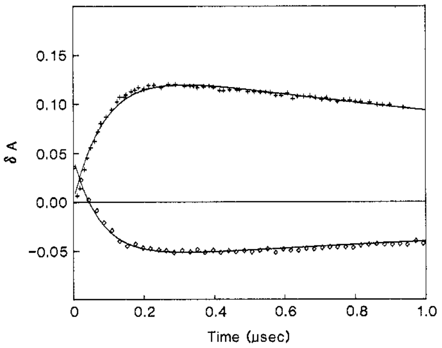

Fig. 2. Change in absorbance (δ*A*) at 540 nm (+) and 440 nm (◇) as a function of time after the laser flash for $4.3 \times 10^{-6}M$ **2** in deoxygenated benzene solution. The solid line in each case is the least-squares best fit of the function $\delta A(\lambda) = [PC]\varepsilon_{PC}(\lambda) + [^3PC]\varepsilon_{^3PC}(\lambda) + [P^3C]\varepsilon_{P^3C}(\lambda)$ with the following estimates for extinction coefficients: $\varepsilon_{PC}(440) = 90{,}000M^{-1}$ cm^{-1}, $\varepsilon_{PC}(540) = 12{,}000M^{-1}$ cm^{-1}, $\varepsilon_{^3PC}(440) = 158{,}000M^{-1}$ cm^{-1}, $\varepsilon_{^3PC}(540) = 15{,}200M^{-1}$ cm^{-1}, $\varepsilon_{P^3C}(440) = 0$, and $\varepsilon_{P^3C}(540) = 224{,}800M^{-1}$ cm^{-1}. Here PC symbolizes the ground state of **2**, ^{3}PC represents **2** with the porphyrin moiety in the lowest triplet state and the carotene moiety in the ground state, and P^{3}C vice versa. Rate equations describing the photophysical processes $^3PC \rightarrow P^3C$ and $P^3C \rightarrow PC$ with rate constants k_1 and k_2, respectively, were solved for the concentrations of PC, ^{3}PC, and P^{3}C as functions of time, and the best values of k_1 and k_2 were extracted. The plot of δ*A* at 540 nm yields $k_1 = 1.1 \times 10^7$ sec^{-1} and $k_2 = 4.1 \times 10^5$ sec^{-1}, and the plot of δ*A* at 440 nm yields $k_1 = 1.3 \times 10^7$ sec^{-1} and $k_2 = 4.2 \times 10^5$ sec^{-1}.

Support for this interpretation comes from studies of singlet energy transfer (antenna function) in these molecules. Singlet-singlet energy transfer from the carotenoid moiety of **1** to the porphyrin occurs with ~ 25 percent efficiency in solution (*2*) and in EPA glass at 77 K, whereas no significant singlet transfer can be detected in fluorescence excitation studies of **2**. The carotenoid singlet lifetime is ultrashort (< 10^{-12} second) (*1*, *6*), and thus internal conversion in the carotenoid moiety is rapid relative to the large-amplitude molecular motions necessary to bring the two π-electron systems into contact. Therefore singlet-singlet transfer is favorable for **1**, which is in a folded conformation before excitation, but unfavorable for **2**, which is in an extended conformation.

This observation of a motional requirement for intramolecular energy transfer sheds further light on the structural requirements for photoprotection and antenna function in biological systems. Our previous work (*1*, *2*) indicated that singlet energy transfer efficiencies approaching 100 percent, which are found in some plant systems (*7*), require a very specific and intimate arrangement of chromophores (such as occurs in **1**) before excitation. This conclusion is consistent with recent studies of natural systems (*8*). The results of the present study suggest that a similar structural arrangement of pigments is necessary for photoprotection through quenching of chlorophyll triplets, but that the relatively long triplet lifetime allows more time for the molecule to assume such a conformation. Thus photoprotective function may, in principle, tolerate significant molecular motion. However, the carotenoid and chlorophyll pigments in natural photosynthetic assemblies are held in place by strong noncovalent interactions with membrane proteins. Large-amplitude motions by the carotenoid and chlorophyll molecules are probably much more restricted in their natural environment than in solution. Thus if a carotenoid is not in a favorable relationship with a chlorophyll molecule before generation of the triplet, it will not be able to compete favorably for it with the small, mobile oxygen molecule.

The observation that antenna function and photoprotection both ultimately require very close approach of chromophores is germane to recent work by Parson and Monger (*9*) with bacterial reaction center preparations. They found that sensitization of the carotenoid triplet ceases at very low temperature (< 20 K) and suggested that temperature-induced structural changes shift the electronic energy levels of the pigments so that population of the carotenoid triplet is unfavorable. Although not reported to date, the persistence of antenna function at these temperatures would strongly support this interpretation. An alternate interpretation, a structural change affecting the orientation and distance between the chromophores, would be indicated by concomitant loss of antenna function at very low temperatures.

These results and those reported previously (*3*) suggest that photoprotection through quenching of the chlorophyll triplet by carotenoids can be extremely effective if protection is accorded to key chlorophyll molecules (such as those in the energy transduction pathway and in the reaction centers) which are likely to undergo intersystem crossing under saturating conditions in vivo. Scavenging of previously formed singlet oxygen by carotenoids (*10*) likely also occurs, but is inherently less efficient because the carotenoid must compete with all other potential reactants for this deleterious species.

Ana L. Moore
Anna Joy
Roderick Tom
Devens Gust
Thomas A. Moore
Department of Chemistry, Arizona State University, Tempe 85287
René V. Bensasson
Laboratoire de Biophysique, INSERM U201, Muséum National d'Histoire Naturelle, 75005 Paris, France
Edward J. Land
Paterson Laboratories, Christie Hospital and Holt Radium Institute, Manchester M20 9BX, England

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Carbyne Forms of Carbon: Do They Exist?

Abstract. *Almost 15 years have passed since carbynes entered the literature as new forms of elemental carbon. They recently attracted attention as possible interstellar dust constituents and as carriers of presolar noble gases in meteorites. Their existence and that of the related mineral chaoite are questioned, and a reevaluation of previous data is suggested.*

In 1967 Kasatochkin *et al.* (*1*) reported the synthesis of a new polymorph of elemental carbon, known as carbyne, with a structure consisting of linear chains of carbon atoms linked by alternating single and triple bonds. In subsequent studies (*2*) the Russian group suggested the existence of two polymorphs, α- and β-carbyne, and proposed a hexagonal crystal structure in which the carbon chains are aligned parallel to the crystallographic *c*-axis. A naturally occurring form of carbon, described in 1968 by El Goresy and Donnay (*3*) and given the mineral name chaoite by El Goresy (*4*), is considered by Whittaker and Kintner (*5*) to belong to the carbyne series. More recently, Whittaker (*6*) reported the synthesis of eight or more polymorphs of carbyne and found several of these occurring as intergrowths in natural graphites (*7*). Carbynes have also been suggested as possible constituents of the interstellar dust (*8*).

Interest in the carbynes was heightened 2 years ago with the report that they are carriers of isotopically anomalous noble gases in carbonaceous chondrite meteorites, including some noble gas components believed to be of presolar origin (*9, 10*). However, recent work by Smith and Buseck (*11, 12*) and by Lumpkin (*13*) casts doubt on the identification of carbyne; these authors find instead that the carbon in such meteorites is predominantly a poorly ordered graphite.

Carbynes have generally been recognized by their characteristic hexagonal [0001] electron diffraction patterns; however, as we pointed out previously (*12*), the sheet silicate minerals give rise to hexagonal diffraction patterns with a similar range of interplanar spacings (*14*). Because of this potential for misidentification and because of the questions raised by the studies of carbon in meteorites, we reexamined some reported occurrences of carbynes, including chaoite. We used a transmission electron microscope (TEM) equipped with an energy-dispersive x-ray spectrometer (EDS) to check the chemical composition of possible carbyne grains.

Chaoite was first discovered as thin (3 to 15 μm wide) lamellae in graphite in a shock-fused gneiss from the Ries meteorite crater (West Germany) (*3*). We obtained a polished section of this material from A. El Goresy, who identified a graphite-chaoite intergrowth for us. Our observations of this sample by reflected light microscopy differ in two respects from the previous account (*3*), so we describe them here. The chaoite lamellae are optically isotropic and have a poorer polish and much lower reflectivity than the graphite. The graphite lamellae stand up slightly in relief, suggesting that chaoite is the softer of the two phases. Our observations concerning the reflectivity and hardness thus differ from those of El Goresy and Donnay (*3*), who described the chaoite as much more strong-